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SYNTHESIS AND PURIFICATION OF SOME ALKYLBIIPHENYLS AND ALKYLBIICYCLOHEXYLS

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SUMMARY

The syntheses of nine monoalkylbiphenyls and five of the corresponding bicyclohexyl derivatives containing 13 to 16 carbon atoms are described, including details of the reactions, the isolation and description of intermediate compounds where possible, and the methods of purification of the final product. Five of the monoalkylbiphenyls have not been previously reported by other investigators. The separation and the purification of the cis and trans isomers of the bicyclohexyl derivatives are also reported for the first time. Physical properties tabulated are melting point, boiling point, index of refraction, density, viscosity, heat of fusion, and heat of combustion. Distillation curves are plotted for the bicyclohexyl compounds, and time-temperature melting curves are plotted for all compounds that could be crystallized. One of these compounds, 2-butylbiphenyl, had two crystalline modifications melting about 4° C apart.

INTRODUCTION

As part of a program to evaluate hydrocarbons as fuel components for high-speed aircraft (reference 1), a group of alkyl-substituted biphenyl compounds and some of their corresponding saturated derivatives were synthesized and purified at the NACA Lewis laboratory. This group consisted of biphenyl compounds substituted in the 2-position by methyl, ethyl, propyl, isopropyl, butyl, sec-butyl, and isobutyl radicals; and in the 3-position by methyl and ethyl radicals. All of these aromatic hydrocarbons with the exception of 2-sec-butylbiphenyl, 2-isobutylbiphenyl, 3-methylbiphenyl, and 3-ethylbiphenyl were catalytically hydrogenated to the corresponding bicyclohexyl compounds. Each of the hydrogenation products contained a mixture of two geometrical isomers, which were separable by fractional distillation.

A literature survey was undertaken to determine any data previously reported on the syntheses and the physical properties of the hydrocarbons considered. Although 2-methylbiphenyl, 2-ethylbiphenyl,

3-methylbiphenyl, and 3-ethylbiphenyl have been synthesized, their physical constants have not been investigated to the extent desired for the purposes of this study and therefore these compounds were included in the present program. The syntheses and the physical properties of 2-propylbiphenyl, 2-isopropylbiphenyl, 2-butylbiphenyl, 2-sec-butylbiphenyl, and 2-isobutylphenyl are reported herein for the first time.

The synthesis of 2-methylbiphenyl by several methods is reported (references 2 to 6), but only one of these methods (reference 6) appears to give a relatively pure product in appreciable yield. The method described in reference 6, which involves the reaction between 2-tolylmagnesium bromide and cyclohexanone followed by dehydration of the carbinol and dehydrogenation of the olefin, gave over-all reported yields of 30 to 50 percent. The same method, giving increased yields of carbinol with increase in reflux time of the Grignard reaction mixture, was used by another investigator (reference 7). The use of this reaction is reported for the synthesis of 3-methylbiphenyl (reference 6), which has also been prepared by the Friedel-Crafts reaction using biphenyl and methyl chloride (reference 8), by the Wurtz-Fittig synthesis from 3-bromotoluene and bromobenzene (reference 9), and by the reaction of m-toluenediazonium chloride with benzene (reference 5).

The synthesis of 2-ethylbiphenyl in 25-percent over-all yield from ethylmagnesium bromide and 2-phenylcyclohexanone followed by dehydration of the carbinol and dehydrogenation of the resulting olefin is described in reference 10. This hydrocarbon has also been prepared (reference 11) in 77-percent over-all yield from 2-biphenylmagnesium iodide and acetaldehyde followed by hydrogenolysis of the resulting carbinol. The synthesis of 2-isopropenylbiphenyl using acetone as the condensing agent and dehydrating the resulting carbinol is reported in reference 12.

The compound 3-ethylbiphenyl has been synthesized from biphenyl and either ethylene, ethyl chloride, or ethyl bromide using the Friedel-Crafts reaction (references 8 and 13).

References to alkylbicyclohexyls are not numerous; however, 2-methylbicyclohexyl and 2-ethylbicyclohexyl have been synthesized (reference 14) by the use of cyclohexylidene-cyclohexanone and the appropriate alkylmagnesium halide. No reference is made to the existence of geometrical isomers in this class of compounds.

The bicyclohexyls reported herein for the first time include the cis and trans isomers of 2-methylbicyclohexyl, 2-ethylbicyclohexyl,

2-propylbicyclohexyl, 2-isopropylbicyclohexyl, and 2-butylbicyclohexyl. Specific assignment of cis and trans configuration could not be made because of the lack of pertinent thermodynamic data, and therefore the isomers are designated simply low boiling and high boiling in each case.

SYNTHESES

The syntheses of five of the alkylbiphenyls described herein have been previously reported by the NACA Lewis laboratory (reference 15) but are included for completeness and comparison.

The 2-methylbiphenyl, 3-methylbiphenyl, and 3-ethylbiphenyl were prepared according to the general method described in reference 6 by using the appropriate cyclohexanone and arylmagnesium halide with certain modifications in the dehydration and dehydrogenation steps.

All of the 2-substituted alkylbiphenyls with the exception of 2-methylbiphenyl could be conveniently prepared from 2-biphenylmagnesium iodide and an appropriate condensing agent, as indicated in reference 11. Because 2-iodobiphenyl may be synthesized in good yields from readily available and inexpensive 2-aminobiphenyl, this method was chosen as a general one. The close proximity between the boiling points of 2-methylbiphenyl and biphenyl, which is formed by hydrolysis of the Grignard reagent, makes their separation impracticable. The use of this reaction for the synthesis of pure 2-methylbiphenyl was therefore not feasible.

The intermediate carbinols were purified in those cases where the compounds were solid at room temperatures. No attempt was made to separate the cis and trans isomers of the olefins that were obtained as intermediates in this investigation.

Direct hydrogenolysis of the carbinols to the corresponding hydrocarbons (reference 11) could not be duplicated by the present investigators. The alternate procedure of dehydration of the carbinol and hydrogenation of the olefin was used. Because of the thermal instability of 2-vinylbiphenyl, 2-ethylbiphenyl was prepared by direct alkylation of the Grignard reagent by using diethyl sulfate as the alkylating agent. Methallyl chloride was used as condensing agent for the synthesis of 2-isobutylbiphenyl because it gave the desired olefin directly without a dehydration step. Ozonization of samples of the purified olefin product showed that a rearrangement of the olefin took place, the double bond shifting from its original position to one of conjugation with the benzene ring.

The alkylbicyclohexyls were conveniently prepared by the catalytic high-pressure hydrogenation of the corresponding alkylbiphenyl compound. The mixtures of geometrical isomers resulting from this treatment were separated by careful fractionation through high-efficiency fractional-distillation columns. The isomers so separated have been designated the low- and high-boiling isomers.

It was found that 2-butylbiphenyl could be crystallized in either of two modifications, which have melting points about 4° C apart. The conditions required for obtaining one modification or the other were not ascertained. The time-temperature melting curve (fig. 1) was obtained by first determining the melting curve for the lower-melting modification, then recooling and seeding the same sample with a crystal of the higher-melting modification and determining the melting curve as before, thus obtaining two distinct melting plateaus for the same material.

PURIFICATION AND DETERMINATION OF PHYSICAL PROPERTIES

The alkylbiphenyls reported in this report have been prepared in approximately 500-milliliter quantities having a purity greater than 99 mole percent (assuming the impurity is liquid-soluble and solid-insoluble), as evidenced by time-temperature melting curves that were determined for all of the compounds with the exception of 2-isobutylbiphenyl, by methods described in reference 16. These curves are plotted in figures 1 and 2. Final purification of each hydrocarbon consisted generally of fractional distillation through 6-foot glass columns (22-mm I.D.) packed with 3/16-inch glass helices at reduced pressures (15 to 20 mm). If this distillation failed to produce the required purity, distillations were conducted in 6-foot Podbielniak columns at 20 millimeters pressure. Repeated fractionation of 2-isobutylbiphenyl through a Podbielniak column failed to produce any material that could be crystallized and therefore combination of fractions was made on the basis of constant values of density and index of refraction.

Inability to crystallize any of the low-boiling isomers of the alkylbicyclohexyls, with the exception of 2-methylbicyclohexyl, made it impossible to calculate an estimated percent purity for these isomers. In the case of those compounds that could be crystallized, the melting curves (fig. 3) again gave evidence of purities of 99 mole percent or better.

The physical constants listed in tables I and II were determined as follows: The melting points were obtained from the melting curves

according to the graphical method described in reference 17. The densities were determined by use of a specific-gravity balance (reference 18), and the boiling points were determined by use of a platinum-resistance thermometer in an apparatus similar to that described in reference 19, except that the system was pressurized with dry air from a surge tank and held constant by adjusting a continuous bleed. The refractive indices were determined in a Bausch and Lomb precision oil model refractometer, and the standard A.S.T.M. procedures designated in tables I and II were followed in the determination of heats of combustion and of viscosities. The heats of fusion were obtained by use of a method and an apparatus similar to those described in reference 20. The estimated mole-percent purities determined according to methods described in reference 21 are also included. The magnitude of the uncertainties and the precision of the measurements are estimated, respectively, as follows: melting points, 0.02° and $\pm 0.003^{\circ}$ C; boiling points, 0.1° and $\pm 0.04^{\circ}$ C; densities, 0.00005 and ± 0.00002 to ± 0.00003 gram per milliliter; refractive indices, 0.0002 and ± 0.0001 ; kinematic viscosities, 0.5 and ± 0.2 percent of determined value relative to 1.007 centistokes for water at 20° C; heat of fusion, 5 and ± 2.5 percent of determined value.

EXPERIMENTAL DETAILS

A detailed description of each of the reactions involved in the synthesis of the hydrocarbons considered is presented in the following paragraphs:

2-Methylbiphenyl

1-(2-Tolyl)-1-cyclohexanol. - In a 30-gallon glass-lined reactor, 6870 grams (40.2 moles) of o-bromotoluene (Dow Chemical Co., fractionated) was reacted with 990 grams (40.7 gram atoms) of magnesium turnings in 38 liters of absolute ether. To the solution of the o-tolylmagnesium bromide was gradually added 20 liters of an ether solution of 4000 grams (40.8 moles) of cyclohexanone. The reaction mixture was refluxed overnight with stirring and then hydrolyzed with 40 liters of a saturated aqueous ammonium chloride solution. The ether layer was siphoned from the sludge, washed twice with 40-liter portions of water, and then concentrated on the steam bath. Because of its tendency to dehydrate readily, the carbinol was not fractionated but merely distilled at low pressure. The bulk of the material boiled at 117° to 119° C at 2 millimeters and weighed 4605 grams (60-percent yield based on o-bromotoluene).

1-(2-Tolyl)-1-cyclohexene. - A solution of 4140 grams (21.8 moles) of 1-(2-tolyl)-1-cyclohexanol in an equal volume of toluene was slowly passed through a pyrex column, 2.5 by 120 centimeters, packed with activated alumina, 8 to 14 mesh, at 250° to 275° C. After the aqueous layer (385 grams) was separated from the condensate, the toluene was stripped and the residue distilled to give 3520 grams (94 percent based on pure carbinol) of olefin boiling at 75° C at 1 millimeter. The distillate was fractionated; the bulk of the material boiled at 127.5° C at 20 millimeters and had an index of refraction n_D^{20} 1.5438.

2-Methylbiphenyl. - A solution of 1315 grams (7.6 moles) of 1-(2-tolyl)-1-cyclohexene in 2.5 liters of toluene was passed three times through a quartz column, 2.5 by 120 centimeters, packed with chromia-alumina pellets as catalyst and maintained at a temperature of 450° to 475° C. The time for each pass was about 2 hours. Too rapid a rate of addition resulted in insufficient dehydrogenation, whereas a slow addition rate caused the formation of large amounts of fluorene through cyclodehydrogenation. After the toluene was removed, the residue was distilled at reduced pressure to give 1030 grams (80 percent based on pure olefin) of crude hydrocarbon. The refractive index n_D^{20} of the various fractions ranged from 1.585 to 1.591. Several careful fractionations, the final one through a Podbielniak column, were required in order to obtain material of the desired purity with the physical properties listed in table I. The yield of this pure material was approximately 32 percent (based on pure olefin).

2-Ethylbiphenyl

2-Iodobiphenyl. - In a typical experiment, a suspension of 2-aminobiphenyl hydrochloride was prepared by adding 2535 grams (15 moles) of the molten amine (Monsanto Chemical Co., 95 percent purity; melting point, 47° to 49° C) to a vigorously stirred solution of 8.18 kilograms (80 moles HCl) of concentrated hydrochloric acid and 9 liters of water in a 30-gallon glass-lined reactor. When the mixture became homogeneous, the temperature was lowered to 0° to 5° C by the addition of crushed ice, and 3.78 liters of a chilled aqueous solution containing 1092 grams (15.8 moles) of sodium nitrite was added gradually until a positive test for nitrous acid was obtained. Throughout the diazotization the temperature was maintained below 5° C by the addition of crushed ice as required. To the cold solution of the diazonium salt there was added slowly 3.78 liters of a chilled aqueous solution of 2506 grams (15.1 moles) of potassium iodide. Stirring was continued for 15 minutes after the addition was complete, and the reaction mixture was allowed

to come to room temperature and stand overnight. The mixture was heated with stirring until the nitrogen evolution ceased, then cooled, and the organic layer was drawn from the reactor. The product was washed with dilute caustic solution, dried, distilled, and fractionated at reduced pressure to give 2625 grams of 2-iodobiphenyl (63 percent based on pure 2-aminobiphenyl) with a boiling point of 176.5°C at 21 millimeters and n_D^{20} 1.6615. In another similar run a yield of 3220 grams (77 percent) of distilled product was obtained.

2-Biphenylmagnesium iodide. - In a typical reaction, 5 gallons of an ether solution containing 11,200 grams (40 moles) of 2-iodobiphenyl was reacted with 973 grams (40 gram atoms) of magnesium turnings covered with 5 gallons of dry ether in a 30-gallon glass-lined reactor. After the reaction was started, vigorous reflux was maintained by controlling the rate of addition of the halide. Stirring was continued throughout the course of the reaction, which was considered completed 1 hour after all the halide solution had been added.

2-Ethylbiphenyl. - To a solution of 40 moles of 2-biphenylmagnesium iodide, in 38 liters of dry ether in a 30-gallon glass-lined reactor there was added 20 liters of an ether solution containing 12,340 grams (80 moles) of diethyl sulfate. The reaction mixture was refluxed 3 hours with stirring after the addition was completed and then hydrolyzed with 20 liters of a 10-percent hydrochloric acid solution. The ether solution was washed once with 20 liters of dilute sodium bicarbonate solution, twice with equal volumes of water, and the ether stripped. The residue was transferred to a stainless-steel reactor and refluxed 5 hours with 20 liters of 10-percent sodium hydroxide in 50-percent ethanol to destroy the excess diethyl sulfate. The product was separated by diluting the mixture with water, washed twice, and distilled at reduced pressure. By chilling the distillate, biphenyl was crystallized out and 1360 grams was removed by filtering the chilled mixture. The filtrate was fractionated in a high-efficiency vacuum column, and an additional 1150 grams of biphenyl was separated in the initial fractions. This amount represents a 40-percent yield of biphenyl. By continuing the distillation 3056 grams (42 percent based on 2-iodobiphenyl) of pure 2-ethylbiphenyl was isolated.

2-Propylbiphenyl

Ethyl-(2-biphenyl)carbinol. - To a solution of 18 moles of 2-biphenylmagnesium iodide in 7 liters of dry ether in a 10-gallon glass-lined reactor, there was added 1160 grams (20 moles) of propionaldehyde (Matheson Co., Inc. boiling point, 47° to 49°C) in 7 liters

of absolute ether. The complex was hydrolyzed with 10 liters of dilute hydrochloric acid (1.5 liters concentrated hydrochloric acid) and the aqueous layer was drawn from the reactor. The ether layer was washed with 10 liters of dilute sodium bicarbonate and then with an equal volume of water and the ether evaporated on a steam bath. The carbinol crystallized and was recrystallized from neohexane to give 2000 grams (52 percent based on 2-iodobiphenyl) of nearly colorless crystals. Concentration of the mother liquors and distillation of the residue gave 250 grams of biphenyl and 700 grams of a higher-boiling liquid, which was presumed to be a mixture of carbinol and olefin. A sample of the carbinol recrystallized for analysis melted at 65.1° to 65.3° C.

Analysis - Calculated for $C_{15}H_{16}O$: C, 84.86 percent;
H, 7.60 percent.

Found: C, 84.87 percent; H, 7.62 percent.

1-(2-Biphenyl)-1-propene. - A solution of 2000 grams (9.4 moles) of ethyl-(2-biphenyl) carbinol in 4 liters of toluene was slowly passed through the alumina-packed pyrex column maintained at 275° to 325° C. After removing the aqueous layer from the condensate, the toluene and then the residue were distilled to give 1520 grams (83 percent based on pure carbinol) of olefin with a boiling point of 166° C at 23 millimeters. No attempt was made to separate the geometrical isomers, but the olefin was fractionated and one refractive-index plateau, n_D^{20} 1.6148, with a boiling point of 158° C at 15 millimeters was observed at the end of the distillation.

Ozonization of 1-(2-biphenyl)-1-propene. - A solution of 0.1 mole of the constant-index portion of the olefin dissolved in absolute alcohol was converted to the ozonide in an ozonizer similar to that described in reference 22. The ozonide solution was hydrogenated as described in reference 22 to give the carbonyl compounds. After reduction was completed, the products were fractionated. The lower-boiling portion gave a 2,4-dinitrophenylhydrazone melting at 164° to 165° C after one recrystallization. A sample mixed with an authentic sample of the 2,4-dinitrophenylhydrazone of acetaldehyde melted at 164° to 166° C.

The higher-boiling fraction formed an oxime, which had a melting point of 116° to 117° C.

Analysis - Calculated for $C_{13}H_{11}NO$: N, 7.10 percent.

Found: N, 7.04 and 7.18 percent.

The melting point of the oxime of 2-phenylbenzaldehyde has been reported as $115^{\circ}C$ (reference 23).

This aldehyde also gave a semicarbazone, melting point, 210° to $212^{\circ}C$.

Analysis - Calculated for $C_{14}H_{13}N_3O$: N, 17.56 percent.

Found: N, 17.54 and 17.50 percent.

This analysis establishes the position of the double bond, and the compound is proved to be 1-(2-biphenyl)-1-propene.

2-Propylbiphenyl. - A solution of 685 grams (3.52 moles) of constant-index 1-(2-biphenyl)-1-propene in 1 liter of absolute alcohol was mixed with 85 grams of U.O.P. nickel catalyst and hydrogenated at $75^{\circ}C$ and an initial pressure of 1500 pounds per square inch. After removal of the catalyst and the solvent, the hydrocarbon was distilled to give an essentially quantitative yield of crude material, which was fractionated carefully in a high-efficiency column at 20 millimeters to yield 592 grams (86 percent based on pure olefin) of pure hydrocarbon. A separate hydrogenation of the remainder of the olefin, which did not have a constant index of refraction, yielded a product after fractionation, that was identical to that obtained from the constant-index material.

2-Isopropylbiphenyl

Dimethyl-(2-biphenyl)carbinol. - To a solution of 18 moles of 2-biphenylmagnesium iodide in 7 liters of dry ether in a 10-gallon glass-lined reactor, there was added 1200 grams (20.7 moles) of acetone (Mallinckrodt Chemical Works, analytical reagent) in 7 liters of absolute ether. The reaction mixture was refluxed overnight and then hydrolyzed with 4 liters of a saturated aqueous ammonium chloride solution. The ether layer was siphoned off and the remaining sludge was extracted with an additional 4 liters of ether. The combined ether solutions were concentrated on the steam bath and the carbinol allowed to crystallize. The crude carbinol was recrystallized from neohexane to give 1700 grams (44.5 percent based on 2-iodobiphenyl) of pure carbinol and 450 grams (13 percent) of crude olefin recovered from the solvent. A sample of the carbinol, recrystallized to constant melting point, melted at 72.0° to $72.5^{\circ}C$.

Analysis - Calculated for $C_{15}H_{16}O$: C, 84.86 percent;
H, 7.60 percent.

Found: C, 84.66 percent; H, 7.64 percent.

2-(2-Biphenyl)-1-propene. - A solution of 1500 grams (7.1 moles) of dimethyl-(2-biphenyl) carbinol in 2 liters of toluene was dehydrated as previously described for the 1-(2-biphenyl)-1-propene. After the aqueous layer was separated and the toluene distilled, the residue was distilled at reduced pressure to give 1180 grams of crude olefin, which was fractionated to give 950 grams (71 percent) of olefin with a boiling point of $149^{\circ}C$ at 20 millimeters and n_D^{20} 1.5942. None of the fractions could be induced to crystallize on cooling.

2-Isopropylbiphenyl. - A solution of 800 grams (4.1 moles) of 2-(2-biphenyl)-1-propene in 1 liter of absolute alcohol was mixed with 80 grams of U.O.P. nickel catalyst and hydrogenated at $100^{\circ}C$ and an initial pressure of 1500 pounds per square inch. After the catalyst was filtered and the solvent distilled, the hydrocarbon was distilled to give an essentially quantitative yield of crude product, which was fractionated at reduced pressure. Three fractionations, the final one in a 6-foot Podbielniak column, were required to obtain a 42-percent yield (based on pure olefin) of hydrocarbon of the desired purity.

2-Butylbiphenyl

1-(2-Biphenyl)-1-butene. - To a solution of 18 moles of 2-biphenylmagnesium iodide in 7 liters of dry ether in a 10-gallon glass-lined reactor was added gradually a solution of 1440 grams (20 moles) of *n*-butyraldehyde (technical grade, fractionated and dried) in 7 liters of absolute ether. The reaction mixture was refluxed and stirred overnight, then hydrolyzed with 4 liters of saturated aqueous ammonium chloride solution. The clear ether solution was siphoned off, the remaining sludge was extracted with an additional 4 liters of ether, and the combined ether extracts were concentrated on the steam bath. No crystallization occurred even after standing for several days. The residue was therefore distilled at reduced pressure. Partial dehydration occurred and a total of 2650 grams of crude olefin-carbinol mixture was collected as a yellow viscous liquid. A solution of this mixture in 4 liters of toluene was slowly passed through the alumina-packed pyrex column at $300^{\circ}C$. After the aqueous layer was separated and the toluene distilled, the residue was distilled at reduced pressure giving 2520 grams (67 percent based on 2-iodobiphenyl) of olefin with a boiling point of 148° to $150^{\circ}C$ at 10 millimeters and n_D^{20} 1.6008. This olefin

was fractionated and showed two boiling-point plateaus at 167° and 172° C at 18 millimeters, but the separation was not sharp. All the fractions showed a positive Beilstein test for halogen.

Ozonization of 1-(2-biphenyl)-1-butene. - A sample of the olefin was ozonized as described for 1-(2-biphenyl)-1-propene. The low-boiling portion of the products gave a 2,4-dinitrophenylhydrazone melting at 151.5° to 153.5° C after two crystallizations. A sample mixed with an authentic sample prepared from propionaldehyde melted at 151° to 154° C.

The higher-boiling fragment formed an oxime melting at 116.5° to 118.0° C after one recrystallization and showed no depression when mixed with an authentic sample of the oxime of 2-phenylbenzaldehyde.

This analysis establishes the position of the double bond, and the compound is proved to be 1-(2-biphenyl)-1-butene.

2-Butylbiphenyl. - A solution of 1650 grams (7.9 moles) of 1-(2-biphenyl)-1-butene in a small quantity of absolute alcohol was mixed with 300 grams of U.O.P. nickel catalyst. The relatively large amount of catalyst was required because of the halogen impurity present. The olefin was hydrogenated in a 3-liter bomb at 90° C and an initial hydrogen pressure of 1650 pounds per square inch over a period of 20 hours. After removal of catalyst and solvent, the hydrocarbon was distilled at reduced pressure, yielding 1540 grams (92 percent based on pure olefin) of crude hydrocarbon. This product was carefully fractionated in a high-efficiency column at 20 millimeters.

2-sec-Butylbiphenyl

2-(2-Biphenyl)-butenes. - To a solution of 40 moles of 2-biphenylmagnesium iodide in 38 liters of dry ether in a 30-gallon glass-lined reactor was added a solution of 2880 grams (40 moles) of methylethylketone (Chemical Rubber Co., technical grade) in 20 liters of absolute ether. The reaction mixture was refluxed overnight with stirring and hydrolyzed with 20 liters of saturated aqueous ammonium chloride solution. The ether layer was siphoned from the sludge of magnesium salts and concentrated on the steam bath. Considerable quantities of biphenyl crystallized out. An attempt at distillation of the carbinol at reduced pressures (1 mm) caused partial dehydration to the olefin, and therefore no further effort was made to isolate the pure carbinol. The entire amount of crude product was diluted with an equal volume of toluene and passed through the alumina-packed pyrex column at 260° to 275° C. The toluene was distilled and the residue

fractionated at reduced pressure to give 3255 grams (39 percent based on 2-iodobiphenyl) of crude olefin, which had a boiling range of 149° to 155° C at 15 millimeters and n_D^{20} 1.5856 to 1.5957. No attempt was made to separate or to identify possible geometrical or position isomers.

2-sec-Butylbiphenyl. - A total of 3175 grams (15.2 moles) of 2-(2-biphenyl)-butenes was hydrogenated in four portions. Each portion was dissolved in an equal volume of absolute ethanol, mixed with 12 percent by weight of U.O.P. nickel catalyst and hydrogenated in a 3-liter bomb at 115° C and an initial pressure of 1500 to 2000 pounds per square inch. Hydrogenation was slow; each portion required approximately 24 hours for absorption of the theoretical amount of hydrogen at the indicated temperature. Higher temperatures could not be used because of the possibility of ring hydrogenation. After the catalyst was filtered and the solvent distilled, the products were combined for fractionation at reduced pressure. Three fractionations in a 6-foot Podbielniak column were required to obtain the pure hydrocarbon in approximately 28-percent yield (based on pure olefin).

2-Isobutylbiphenyl

1-(2-Biphenyl)-2-methyl-1-propene. - A solution of 3622 grams (40 moles) of methallyl chloride (3-chloro-2-methyl-1-propene, Shell Chemical Co., 95-percent purity) in 15 liters of absolute ether was added gradually to a stirred solution of 40 moles of 2-biphenylmagnesium iodide in 35 liters of dry ether in a 30-gallon glass-lined reactor. The complex was hydrolyzed with 20 liters of dilute hydrochloric acid. The aqueous layer was drawn from the reactor and the ether layer was washed twice with 20-liter portions of water and then concentrated on the steam bath. A total of 2460 grams (40 percent based on 2-iodobiphenyl) of biphenyl was separated by cooling the residue, filtering the solid, and distilling the filtrate at reduced pressure. Total weight of crude olefin distilled was 3350 grams (40 percent based on 2-iodobiphenyl). A portion of this material was fractionated at reduced pressure. No attempt was made to separate isomers, but one refractive-index plateau at n_D^{20} 1.6004 (boiling point, 132° C at 5 mm and melting point, 32.0° to 33.0° C) was observed at the end of the distillation.

Analysis - Calculated for $C_{16}H_{16}$: C, 92.25 percent;

H, 7.75 percent.

Found: C, 92.19 percent; H, 7.77 percent.

Ozonization of 1-(2-biphenyl)-2-methyl-1-propene. - A sample (0.1 mole) of constant-index olefin was ozonized. The low-boiling portion of the products gave a 2,4-dinitrophenylhydrazone melting at 125.5° to 126.5° C after two crystallizations. A sample mixed with an authentic sample prepared from acetone showed no melting-point depression. The higher-boiling fragment (boiling point, 143° C at 5 mm) formed an oxime melting at 117.5° to 118.0° C, a 2,4-dinitrophenylhydrazone melting at 206° to 207° C, and a phenylhydrazone melting at 125° to 133° C (decomposes). A sample of the oxime mixed with a corresponding sample from the ozonization of 1-(2-biphenyl)-1-propene previously described showed no melting-point depression.

Analysis of the phenylhydrazone -

Calculated for $C_{19}H_{16}N_2$: N, 10.29 percent.

Found: N, 10.33 and 10.27 percent.

The compound is thus proved to be 1-(2-biphenyl)-2-methyl-1-propene and not 3-(2-biphenyl)-2-methyl-1-propene, as expected. A shift of the double bond apparently occurred.

Ozonization of a portion of the low-index material produced the same fragments, which indicates geometrical isomerism.

2-Isobutylbiphenyl. - In a typical experiment, 1040 grams (5 moles) of 1-(2-biphenyl)-2-methyl-1-propene was hydrogenated in a 3-liter bomb at 160° C and an initial pressure of 1500 to 2000 pounds per square inch using 15 to 20 percent by weight of copper chromite catalyst. Several different solvents were tried including ethyl alcohol, dioxane, and methylcyclohexane. The U.O.P. nickel was also investigated as a catalyst in the high-pressure hydrogenations, and Raney nickel and Adams platinum catalyst were tried in small-scale, low-pressure, low-temperature hydrogenations. None of these treatments caused hydrogenation at the rate ordinarily observed in olefinic compounds. Hydrogenation was very slow, as in the case of 2-(2-biphenyl)-butenes, and three careful fractionations through a Podbielniak column of the combined products of hydrogenation from two similar runs were required to yield 300 grams of material having constant refractive-index and density values. None of the fractions could be induced to crystallize.

3-Methylbiphenyl

1-Phenyl-3-methylcyclohexenes. - In a 30-gallon glass-lined reactor, 7065 grams (45 moles) of bromobenzene was reacted with 1095 (45 gram atoms) of magnesium turnings in 25 liters of absolute ether. To the solution of phenylmagnesium bromide was added gradually a solution of 4200 grams of 3-methylcyclohexanone containing 3360 grams (30 moles) of the ketone and 20 percent of 3-methylcyclohexanol in 11 liters of absolute ether. The reaction mixture was refluxed with stirring for 5 hours and then hydrolyzed with 20 liters of dilute hydrochloric acid. No attempt was made to isolate the carbinol in this case. The aqueous layer was drawn from the reactor and the ether solution was concentrated on the steam bath. The residue was passed through an alumina-packed tower at 275° C. After removing the water from the condensate, the benzene (from the hydrolysis of excess phenylmagnesium bromide) was distilled and the residue fractionated at reduced pressure to give 2300 grams (44 percent based on pure 3-methylcyclohexanone) of olefin, which had a boiling point of 139° C at 20 millimeters and n_D^{20} 1.5550.

3-Methylbiphenyl. - A charge of 1465 grams (8.5 moles) of 1-phenyl-3-methylcyclohexenes was slowly passed through a quartz column packed with chromia-alumina pellets as catalyst and maintained at a temperature of 425° to 450° C. The time required for the run was 2 hours. The product was distilled at reduced pressure to give 1260 grams (88 percent based on pure olefin) of crude hydrocarbon. Fractional distillation yielded 1015 grams (71 percent) of pure material with the physical properties listed in table I.

3-Ethylbiphenyl

3-Ethylcyclohexanone. - A total of approximately 17 kilograms (140 moles) of 3-ethylphenol (Reilly Tar & Chemical Corp., 95-percent purity) was hydrogenated in two portions in a 20-liter bomb. The first portion was mixed with 1000 grams of U.O.P. nickel catalyst and hydrogenated at 200° C and an initial pressure of 1500 to 2000 pounds per square inch. The product was decanted, the second portion added with an additional 400 grams of catalyst, and the reaction carried out in a similar manner. The reaction products were filtered, combined, and distilled in 3 to 4 liter portions, which boiled over a range of 190° to 200° C at atmospheric pressure. No attempt was made to separate possible geometrical isomers. Yields were essentially quantitative.

In a typical reaction carried out in a 30-gallon glass-lined reactor, the distilled 3-ethylcyclohexanol was oxidized to 3-ethylcyclohexanone as follows: In 15 gallons of dilute sulfuric acid containing 8.64 kilograms (84 moles) of concentrated sulfuric acid, there was dissolved 10.14 kilograms (34 moles) of sodium dichromate crystals (reagent, $\text{Na}_2\text{Cr}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$). To this stirred cooled solution was added 6400 grams (50 moles) of 3-ethylcyclohexanol at such a rate that the temperature of the reaction mixture did not rise above 30°C . Stirring was continued at room temperature for 2 hours after the addition was completed. The acid layer was then drawn from the reactor and the organic layer was diluted with an equal volume of ether and washed three times with 5-percent aqueous sodium hydroxide solution. The organic layer was washed in 3-liter portions in a 6-liter separatory funnel. The product was dried over anhydrous calcium sulfate and distilled at reduced pressure to give 2635 grams (42 percent based on 3-ethylphenol) of ketone, which had a boiling point of 95°C at 33 millimeters and n_D^{20} 1.4520. The semicarbazone of this material melted at 168° to 169°C and the 2,4-dinitrophenylhydrazone melted at 138° to 139°C .

1-Phenyl-3-ethylcyclohexenes. - The Grignard reagent, phenylmagnesium bromide, prepared in a 30-gallon glass-lined reactor from 7066 grams (45 moles) of bromobenzene and 1095 grams (45 gram atoms) of magnesium turnings in 8 gallons of absolute ether, was condensed with 5678 grams (45 moles) of 3-ethylcyclohexanone in 4 gallons of absolute ether. The reaction mixture was refluxed overnight and then hydrolyzed with 2.5 gallons of saturated aqueous ammonium chloride solution. The ether layer was siphoned from the sludge, which was flushed out of the reactor with hot water. The ether solution was then returned to the reactor, washed twice with 5-gallon portions of water and then concentrated by evaporation under a hood. An attempt at distillation of a portion of the crude carbinol produced partial dehydration. The carbinol appeared to boil, however, at 160°C at 14 millimeters and n_D^{20} 1.5367.

The entire yield of crude carbinol was passed through an alumina-packed pyrex column at 250° to 300°C . The aqueous layer was separated and the crude olefin fractionated at reduced pressure to give 5770 grams (69 percent based on bromobenzene) of olefin, which had a boiling point of 150°C at 17 millimeters and n_D^{20} 1.5508. No attempt was made to locate the position of the double bond.

3-Ethylbiphenyl. - A charge of 1860 grams (10 moles) of 1-phenyl-3-ethylcyclohexenes was slowly passed through a quartz column, packed

with chromia-alumina pellets as catalyst and maintained at a temperature of 450° to 475° C. The product, weighing 1700 grams, was fractionated at reduced pressure, and after removal of a small quantity of biphenyl and some material with a low index of refraction, formed presumably from disproportionation, 1350 grams (74 percent based on pure olefin) of constant-index 3-ethylbiphenyl was obtained. The constant-index product from two similar runs was combined and then fractionated in a Podbielniak column to obtain material of the desired purity.

Alkylbicyclohexyls

The alkylbiphenyls used for hydrogenation had physical properties similar to those described in table I. Only material of constant refractive index was used. The quantity of each hydrocarbon hydrogenated varied according to the amount available for such use. Hydrogenations were carried out in a 3-liter bomb at initial hydrogen pressures of 1500 to 2000 pounds per square inch and temperatures of 190° to 210° C. A volume of methylcyclohexane equal to that of the hydrocarbon was used as solvent, and 10 to 12 percent by weight of U.O.P. nickel was used as catalyst, except for the 2-butyl hydrocarbon. Small amounts of halogen-containing olefin were included in this hydrogenation and therefore 18 to 20 percent by weight of U.O.P. nickel was required in this case.

The quantities of material hydrogenated were as follows:

	(grams)	(moles)
2-Methylbiphenyl	2590	15.4
2-Ethylbiphenyl	1925	10.6
2-Propylbiphenyl	1100	5.6
2-Isopropylbiphenyl	950	4.8
2-Butylbiphenyl	1015	4.8

Yields of completely hydrogenated product were essentially quantitative. Any traces of aromatics were removed by passage of the hydrogenation products, after distillation of the solvent, through silica-gel columns. Careful fractionation at reduced pressure through 6-foot Podbielniak distillation columns succeeded in separating the isomeric mixtures into their pure components. The distillation curves for the alkylbicyclohexyls obtained by hydrogenating the alkylbiphenyls are shown in figure 4. The physical properties of these hydrocarbons are listed in table II with the approximate relative yields of each isomer.

CONCLUDING REMARKS

The syntheses and the purification of nine monoalkylbiphenyls and the bicyclohexyl derivatives of five of them were described. Five of the monoalkylbiphenyls were reported for the first time. These compounds include 2-propylbiphenyl, 2-isopropylbiphenyl, 2-butylbiphenyl, 2-sec-butylbiphenyl, and 2-isobutylbiphenyl. Separation and purification of the ten geometrical isomers of the bicyclohexyl derivatives were also reported for the first time. These are the cis and trans isomers of 2-methylbicyclohexyl, 2-ethylbicyclohexyl, 2-propylbicyclohexyl, 2-isopropylbicyclohexyl, and 2-butylbicyclohexyl.

Physical properties were tabulated and time-temperature melting curves plotted for all the compounds that could be crystallized. It was found that 2-butylbiphenyl could be crystallized in either of two modifications, which had melting points about 4° C. apart.

National Advisory Committee for Aeronautics,
Lewis Flight Propulsion Laboratory,
Cleveland, Ohio, August 1, 1950.

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TABLE I - PHYSICAL PROPERTIES OF ALKYLBIIPHENYLS

Hydrocarbon	Melting point (°C)	Boiling point at 760 mm (°C)	Index of refraction _D ²⁰	Density at 20 (grams/ml)	Heat of fusion ΔH_f (kcal/mole)	Estimated purity (mole percent)	Net heat of combustion ^a (kcal/mole)	Analyses (percent)				Viscosity ^b (centistokes)			
								Carbon		Hydrogen		0° C (32° F)	37.78° C (100° F)	60° C (140° F)	98.89° C (210° F)
								Calcu-Found	lated	Calcu-Found	lated				
2-Methylbiphenyl	-0.20	255.30	1.5914	1.01134	3.1	99.3	1800	92.81	92.82	7.19	7.08	13.27	3.19	----	1.06
2-Ethylbiphenyl	-6.13	265.97	1.5905	.99671	3.9	99.9	1740	92.26	92.32	7.74	7.57	13.94	3.44	----	1.17
2-Propylbiphenyl	-11.26	277.22	1.5896	.98018	4.9	99.8	1885	91.78	91.63	8.22	8.18	22.41	4.44	----	1.33
2-Isopropylbiphenyl	24.46	269.77	1.5703	.98227	4.5	99.8	1885	91.78	91.73	8.22	8.17	Solid	5.76	----	1.46
2-Butylbiphenyl	-13.71	291.20	1.5604	.96763	5.5	99.1	2030	91.37	91.40	8.53	8.51	24.66	4.87	----	1.43
2-sec-Butylbiphenyl	-9.65														
2-Propylbiphenyl	8.12	281.75	1.5622	.97145	4.9	99.0	2055	91.37	91.36	8.63	8.61	Solid	7.09	3.52	1.60
2-Isobutylbiphenyl	Class	282.13	1.5583	.96318	---	---	2035	91.37	91.41	8.63	8.56	48.72	6.02	3.17	1.48
3-Methylbiphenyl	4.53	272.70	1.6039	1.01394	4.6	99.4	1590	92.81	92.71	7.19	7.18	13.21	3.23	1.98	1.09
3-Ethylbiphenyl	-27.57	285.96	1.5930	.99932	4.0	99.8	1750	92.26	92.20	7.74	7.60	12.17	3.40	2.13	1.19

a. S.T.M. procedure: D240-39.

b. A.S.T.M. procedure: D445-46F.

TABLE II - PHYSICAL PROPERTIES OF ALKYLBIICYCLOHEXYLS

Hydrocarbon	Melting point (°C)	Boiling point at 760 mm (°C)	Index of refraction _D ²⁰	Density at 20 (grams/ml)	Heat of fusion ΔH_f (kcal/mole)	Estimated purity (mole percent)	Net heat of combustion ^a (kcal/mole)	Relative yield of each isomer (percent)	Analyses (percent)				Viscosity ^b (centistokes)			
									Carbon		Hydrogen		0° C (32° F)	37.78° C (100° F)	60° C (140° F)	98.89° C (210° F)
									Calcu-Found	lated	Calcu-Found	lated				
2-Methylbicyclohexyl ^c	-26.43	249.87	1.4791	0.88447	4.4	98.9	1855	41	86.58	86.65	13.42	13.35	8.84	3.11	2.08	1.22
2-Ethylbicyclohexyl ^d	-10.27	255.00	1.4836	.89450	4.6	99.2	1870	59	86.58	86.58	13.42	13.41	12.82	4.20	2.69	1.51
2-Propylbicyclohexyl ^d	Class	266.23	1.4827	.89065	---	---	1995	34	86.51	86.60	13.49	13.48	16.33	4.20	2.58	1.40
2-Isopropylbicyclohexyl ^d	-0.35	269.54	1.4851	.89624	5.4	99.9	2015	66	86.51	86.46	13.49	13.47	18.53	4.75	2.89	1.54
2-Butylbicyclohexyl ^d	Class	279.40	1.4807	.88527	---	---	2145	35	86.46	86.44	13.54	13.56	28.32	5.58	3.05	1.56
2-sec-Propylbicyclohexyl ^d	0.25	282.22	1.4838	.89205	5.7	99.8	2160	65	86.46	86.47	13.54	13.56	34.08	6.20	3.46	1.71
2-Isobutylbicyclohexyl ^d	Class	277.18	1.4843	.89305	---	---	2140	49	86.46	86.45	13.54	13.54	46.82	6.94	3.75	1.80
2-Isopropylbicyclohexyl ^d	-9.13	283.06	1.4901	.90365	5.7	99.9	2165	51	86.46	86.50	13.54	13.53	29.12	6.54	3.78	1.91
2-Butylbicyclohexyl ^d	Class	294.15	1.4799	.88227	---	---	2300	40	86.40	86.42	13.60	13.48	42.37	6.74	3.64	1.76
2-sec-Butylbicyclohexyl ^d	-6.51	296.56	1.4827	.89819	6.5	---	2300	60	86.40	86.44	13.60	13.48	51.18	7.65	4.05	1.91

a. S.T.M. procedure: D240-39.

b. A.S.T.M. procedure: D445-46F.

C. Low-boiling isomer.

D. High-boiling isomer.

Because of short length of equilibrium portion of melting curve for this compound, estimate of purity according to reference method was not deemed valid.

NACA

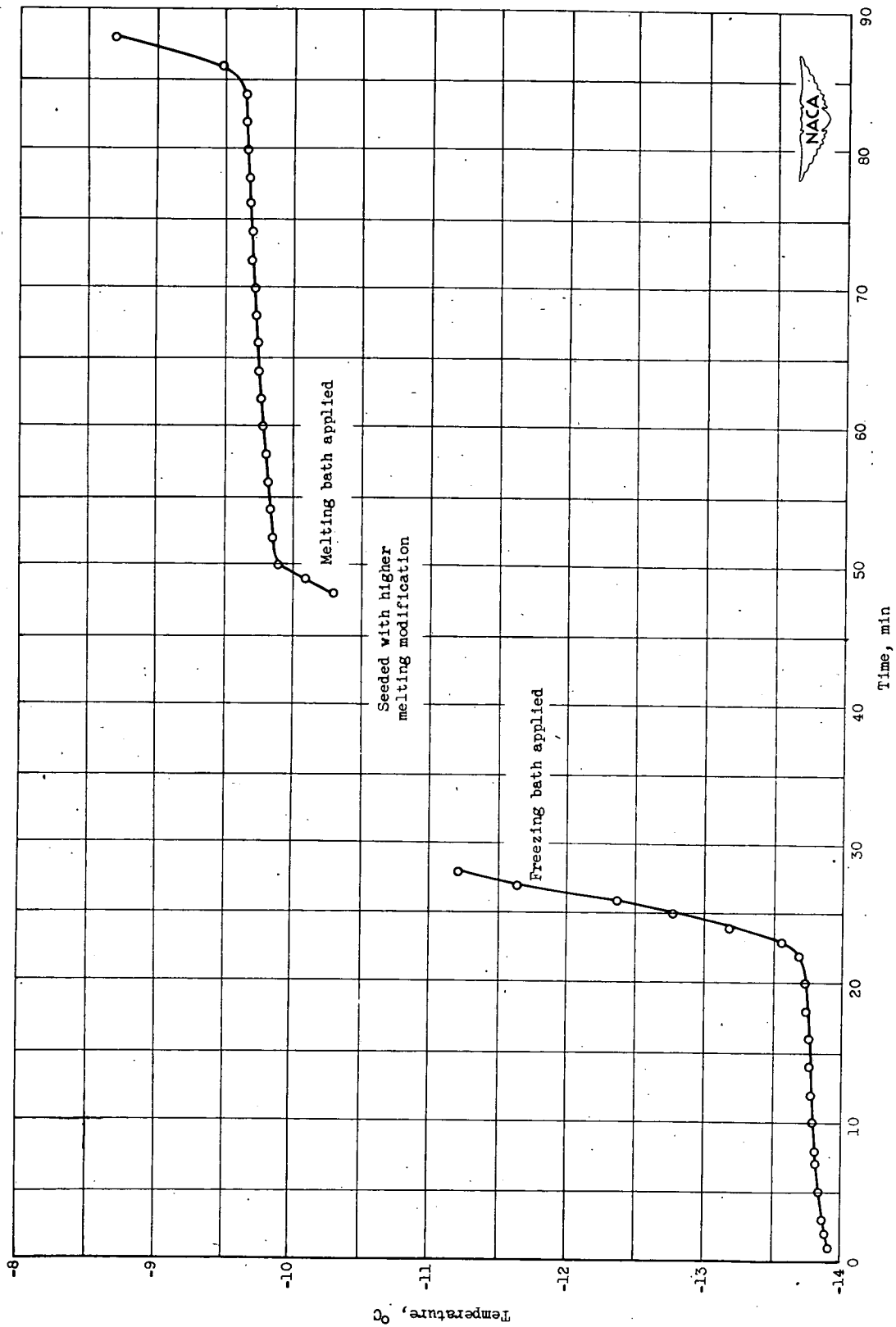


Figure 1. - Time-temperature melting curves for two crystalline modifications of 2-butylbiphenyl.

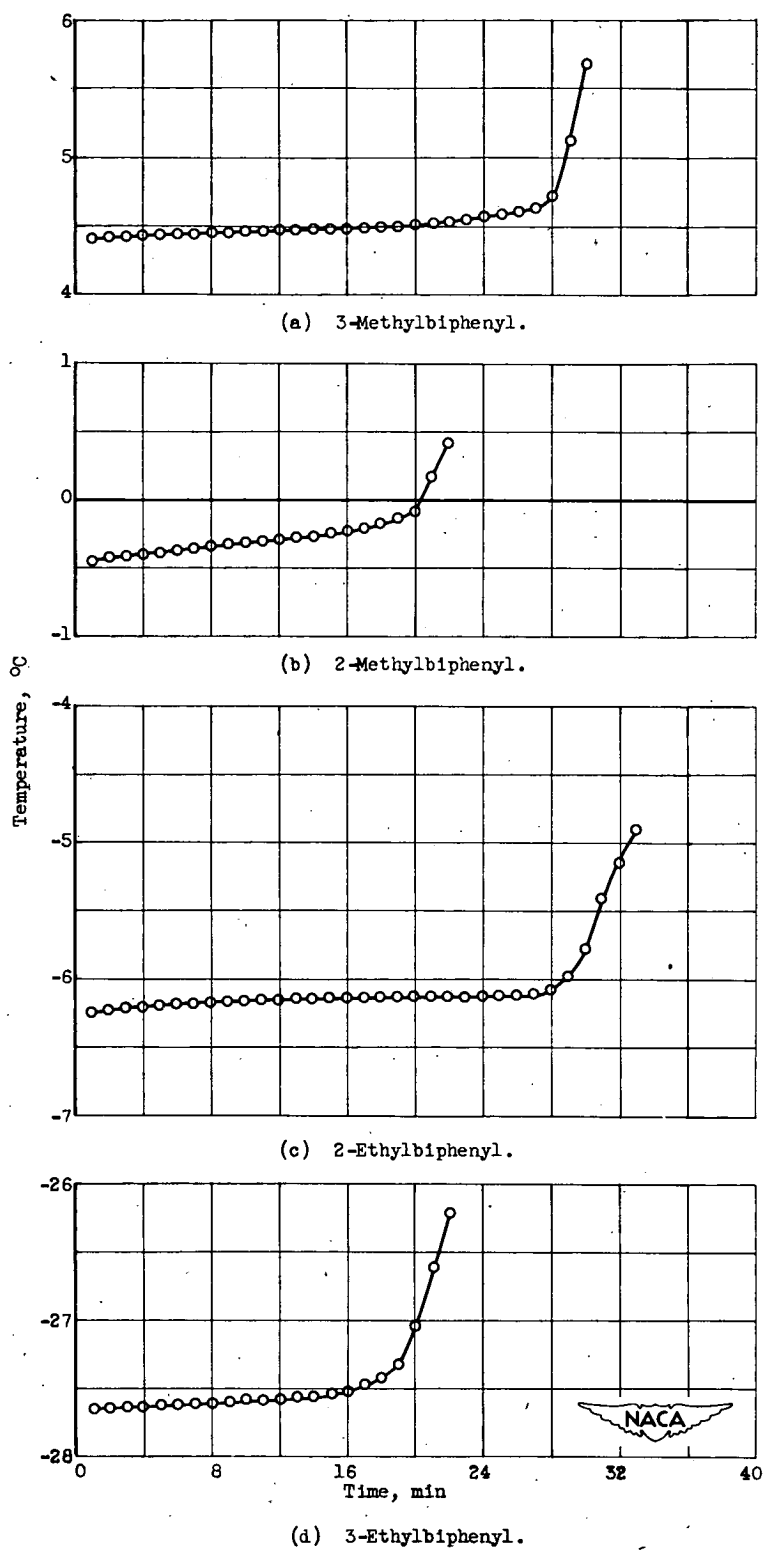
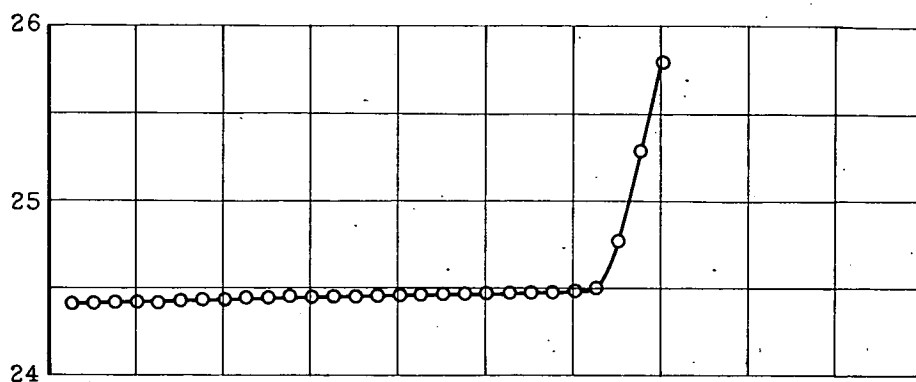
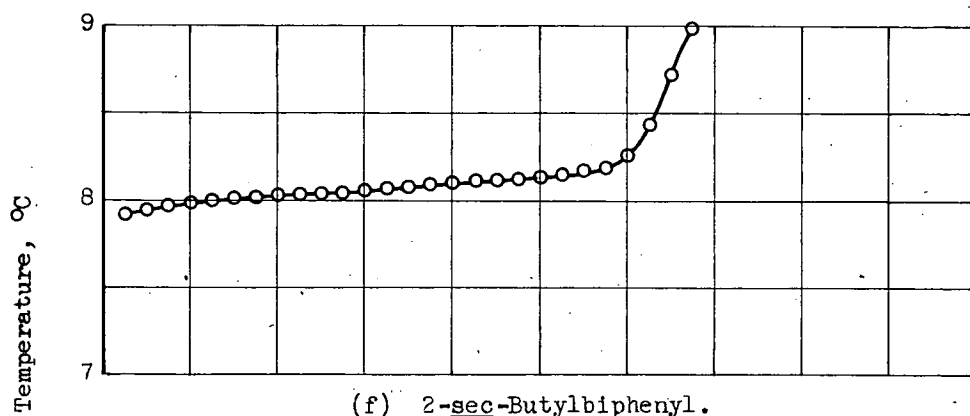
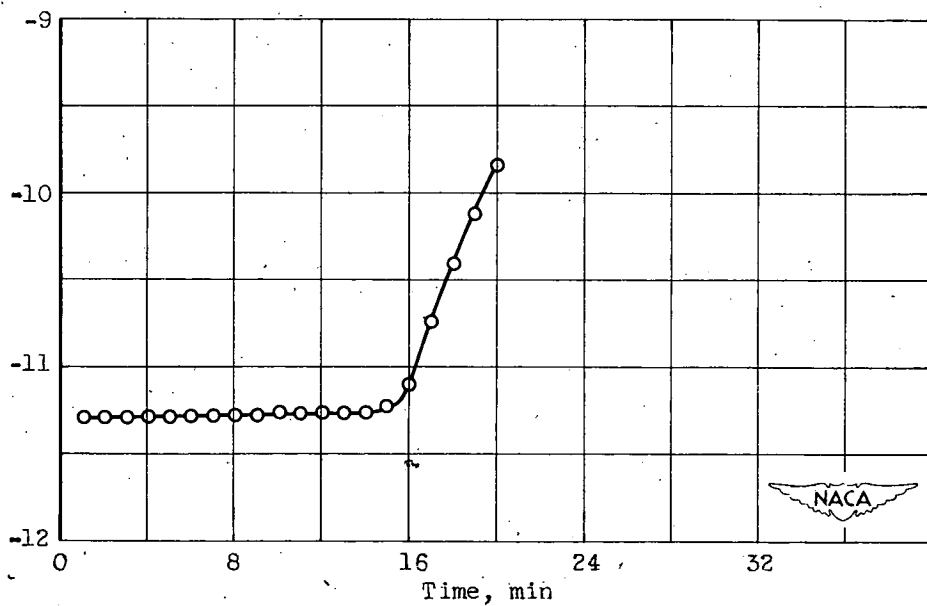


Figure 2. - Time-temperature melting curves for various alkylbiphenyls.

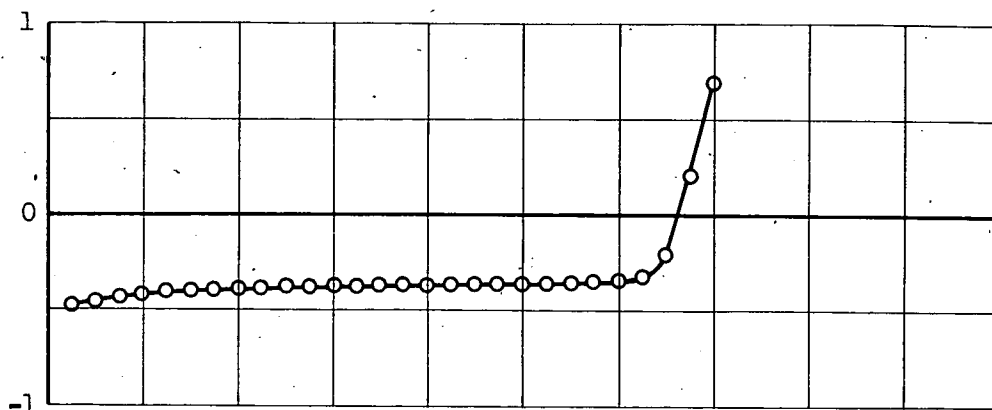


(e) 2-Isopropylbiphenyl.

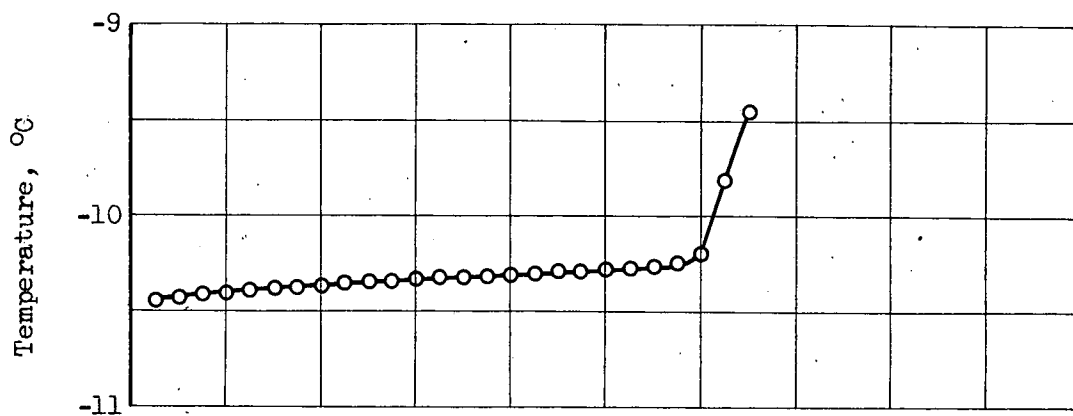
(f) 2-sec-Butylbiphenyl.

(g) 2-Propylbiphenyl.

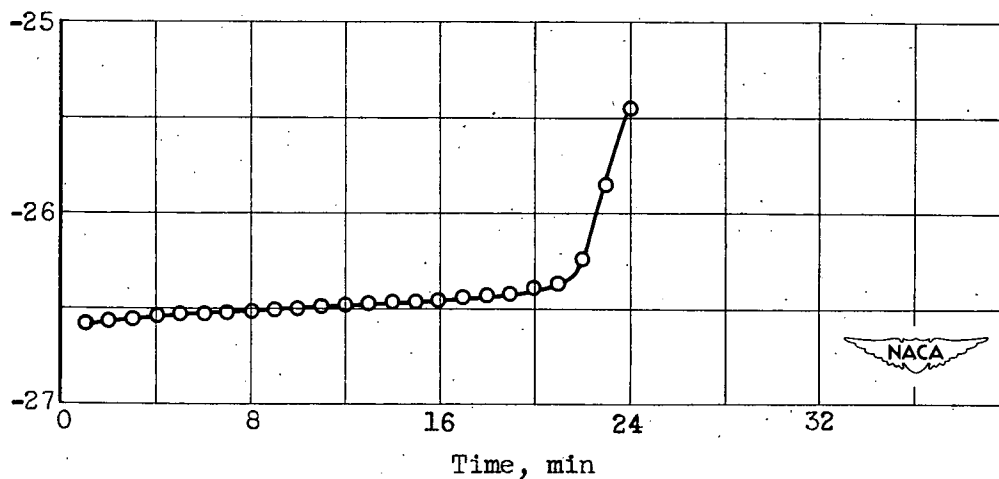
Figure 2. - Concluded. Time-temperature melting curves for various alkylbiphenyls.



(a) 2-Ethylbicyclohexyl (high boiling).

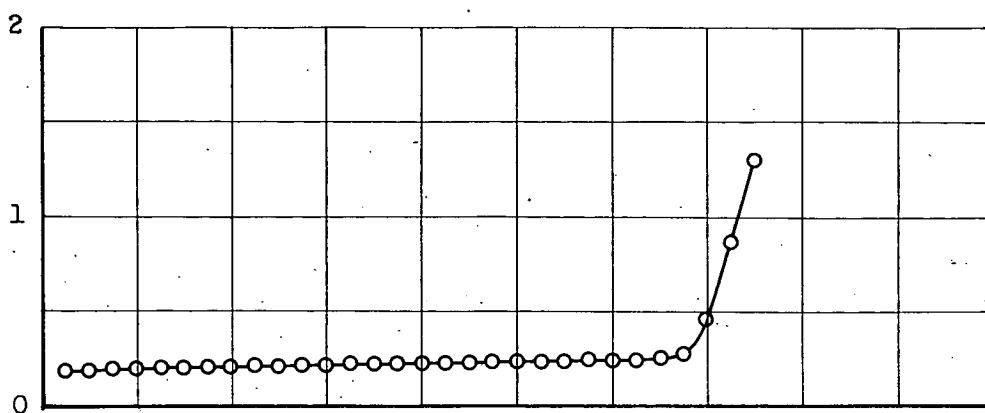


(b) 2-Methylbicyclohexyl (high boiling).

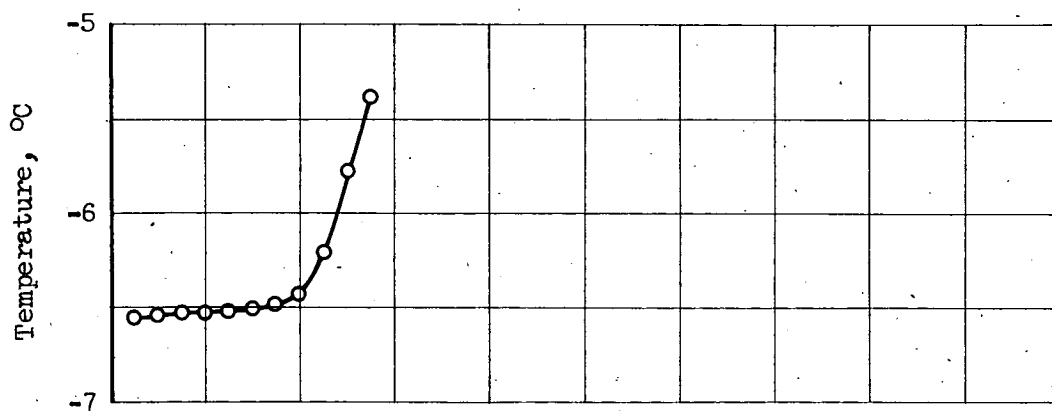


(c) 2-Methylbicyclohexyl (low boiling).

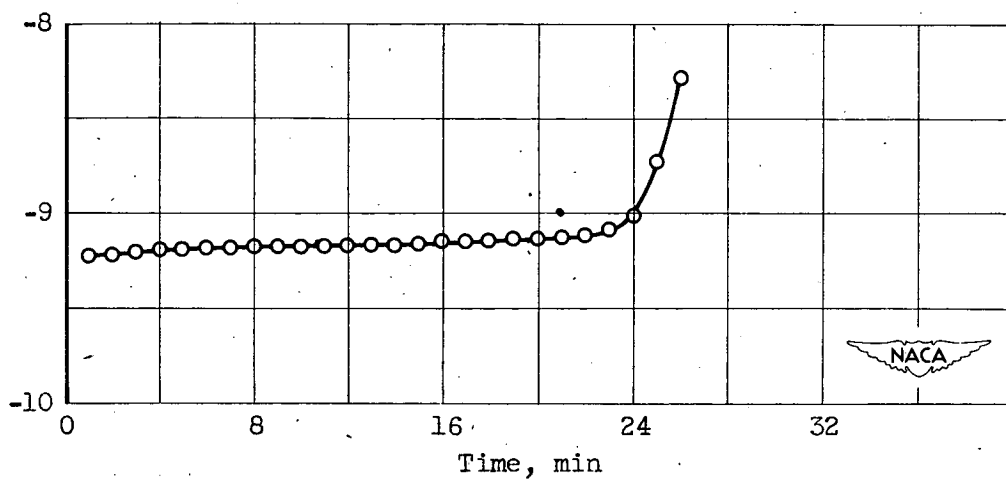
Figure 3. - Time-temperature melting curves for various alkyl-bicyclohexyls.



(d) 2-Propylbicyclohexyl (high boiling).

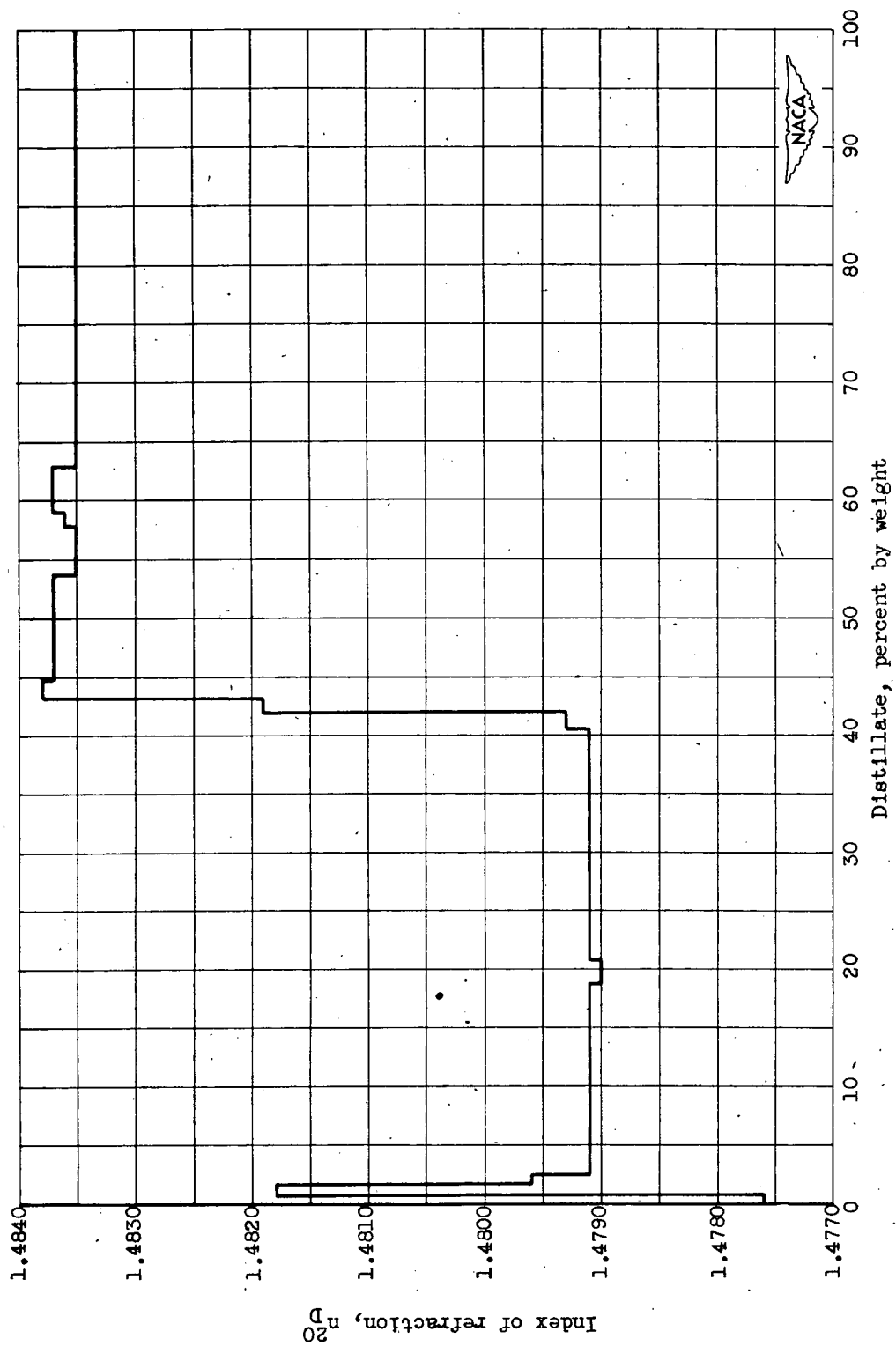


(e) 2-Butylbicyclohexyl (high boiling).



(f) 2-Isopropylbicyclohexyl (high boiling).

Figure 3. - Concluded. Time-temperature melting curves for various alkylbicyclohexyls.



(a) 2-Methylbicyclohexyls.

Figure 4. - Distillation of products from hydrogenation of 2-alkylbiphenyls.

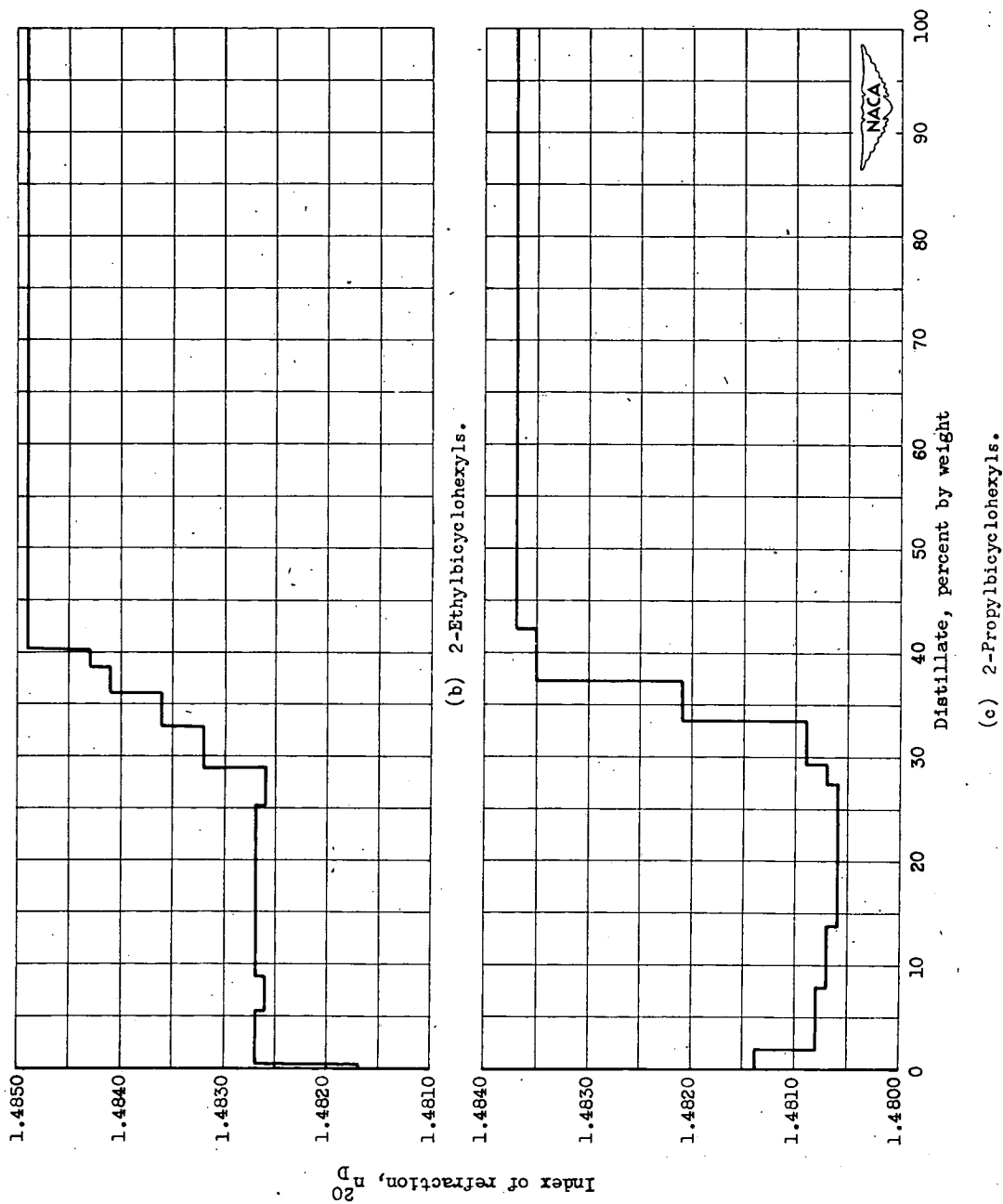
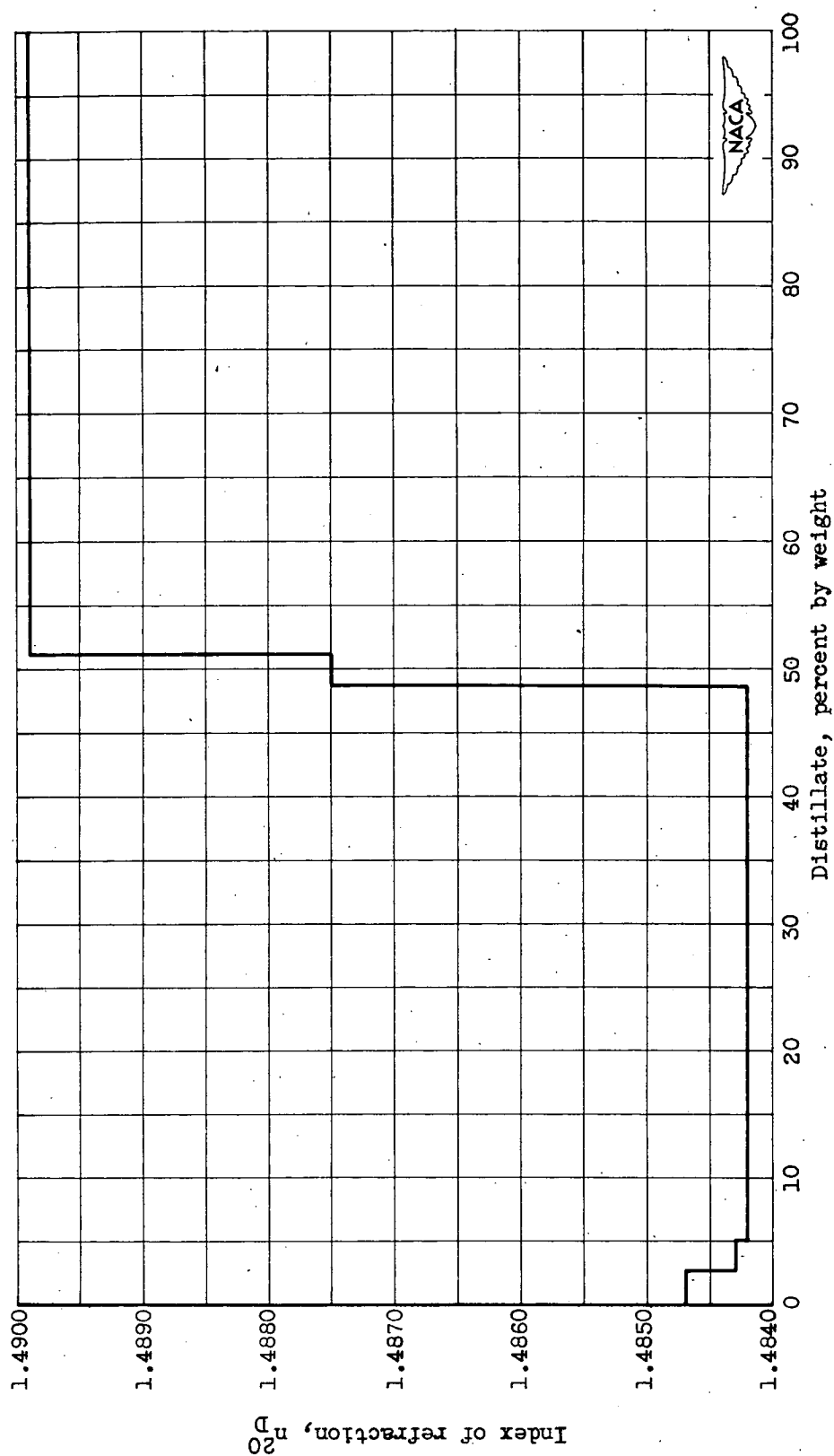
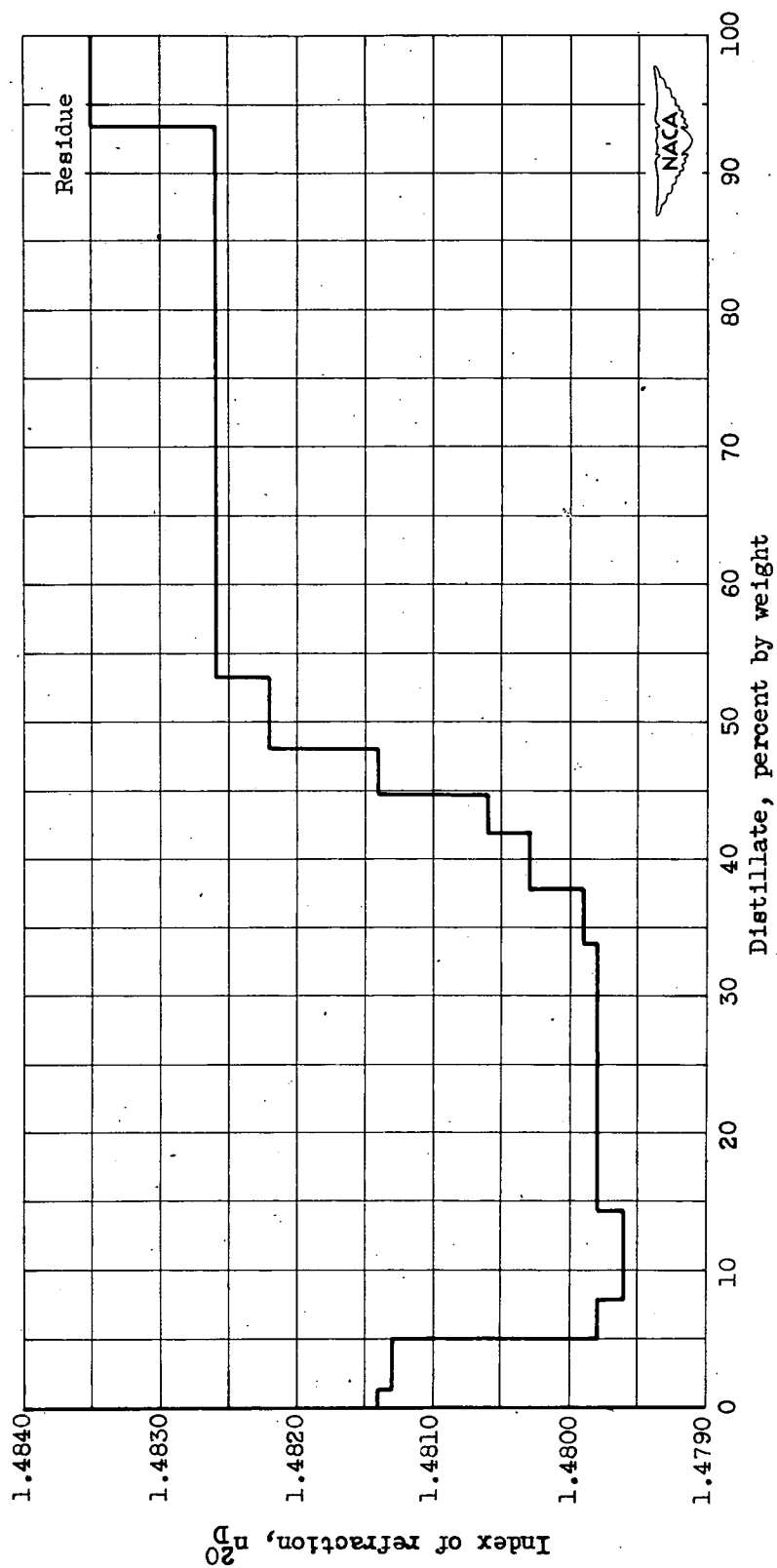


Figure 4. - Continued. Distillation of products from hydrogenation of 2-alkylbiphenyls.



(d) 2-Isopropylbicyclohexyls.

Figure 4. - Continued. Distillation of products from hydrogenation of 2-alkylbiphenyls.



(e) 2-Butylbicyclohexyls.

Figure 4. - Concluded. Distillation of products from hydrogenation of 2-alkylbiphenyls.